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(54) **Organic composite coated steel strip having improved corrosion resistance and weldability**

Mit einem organischen Verbundmaterial beschichtetes Stahlband mit verbesserter Korrosionsbeständigkeit und Schweissbarkeit

Ruban en acier avec un revêtement organique composite et ayant une résistance à la corrosion et une soudabilité améliorées

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EP-A- 0 312 599

- **PATENT ABSTRACTS OF JAPAN vol. 13, no. 84 (C-572)(3432) February 27, 1989 & JP-A-63 270 480**

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Description

This invention relates to organic composite coated steel strip having improved corrosion resistance and weldability mainly used in automobile body components by press forming.

BACKGROUND OF THE INVENTION

In recent years, to meet severer corrosion resistance requirements for automobile bodies, surface treated steel strips in the form of conventional cold rolled steel strips plated with zinc or zinc base alloy are often used. Particularly in the area where corrosion is a serious problem, high bare corrosion resistance is needed in internal strip configurations including internal cavity-defining structures and bends where protective coatings after pressing and body assembly cannot fully cover. Organic composite coated steel strips having chromate and organic coatings on a zinc plated steel substrate were developed to meet such needs as disclosed in Japanese Patent Application Kokai Nos. 108292/1982 and 224174/1983.

These proposals intend to provide high corrosion resistance by coating a zinc plated steel substrate with a coating composition containing a resin and a water dispersed silica sol. However, the use of water dispersed silica sol gives rise to several problems including (1) limitation of the available type of organic resin binder which has to be compatible with the silica sol, (2) the presence of residual water-soluble components in the coating which allow water to penetrate into the coating during subsequent chemical conversion treatment so that chromium in the underlying chromate layer can dissolve out to contaminate the environment, (3) potential separation of the coating during alkali degreasing which can lead to a loss of corrosion resistance, and (4) poor adherence of the coating in that water can penetrate underneath the coating upon exposure to a corrosive environment, allowing the water soluble components to dissolve therein and exhibit high alkalinity cleaving the interfacial bond between the coating and the chromate. These problems are essentially derived from the use of water as the solvent for the coating compositions.

One solution is disclosed in Japanese Patent Application Kokai No. 22637/1988 which uses a coating composition comprising a hydrophobic silica obtained by subjecting silica on its surface to organic substitution in an organic solvent and an epoxy resin having a primary hydroxyl group and a basic nitrogen atom added thereto. Although compatibility is maintained between silica sol and the organic resin and improved adherence after coating is achieved, this coating has no ability to hold corrosion products stably because of the absence of a free silanol group on the silica surface. Therefore, corrosion resistance is materially low. The use of existing silica sol of either a water or organic solvent system adversely affects weldability.

Further, Japanese Patent Application Kokai Nos. 35798/1988 and 65179/1989 discloses addition of dry fumed silica to organic solvents. Although corrosion resistance and weldability are improved, the use of fumed silica not only leads to a substantial increase in viscosity of the coating composition which can interfere with control of the coating weight upon its application, but frequently causes aggregation during blending of the coating composition so that the composition cannot be applied.

EP-A-0 298 409 discloses a steel sheet having an organic composite plating layer excellent in press workability, spot weldability, electrodeposition coatability and corrosion resistance which comprises a zinc plated, aluminum plated or zinc base composite alloy plated steel sheet, a first layer of an insoluble chromate film of 5% or less in the content of water-soluble matter formed on the surface of the steel sheet at a coverage of 10-150 mg/m^2 in terms of chromium content and a second layer of a coating composition having the following composition coated at a thickness of 0.3-5 μm as a solid film on said first layer:

(A) a bisphenol type epoxy resin having a number-average molecular weight of 300-100,000 in an amount of 30% by weight or more of solid matter in the coating composition,
(B) at least one polyisocyanate compound or block polyisocyanate compound as a curing agent at a weight ratio to solid matter in the epoxy resin of 1/10-20/10,
(C) fumed silica having an average particle size of 0.1-100 mμ in an amount of 5-50% by weight of solid matter in the coating composition, and
(D) a ketone organic solvent in an amount of 40% by weight or more of the coating composition, and the solid content of the coating composition being 10-50% by weight.

EP-A-0 312 599 discloses a highly corrosion-resistant, surface-treated steel sheet which has in order a zinc or zinc alloy deposit as an undercoating deposit, a chromate coating, and a coating of resin composition comprising a base resin obtained by adding at least one basic nitrogen atom and at least two primary hydroxy groups to the terminal of an epoxy resin, silica, and a difficultly soluble chromium compound. This resin composition has predetermined weight ratios of base resin/silica, base resin/difficultly soluble chromium compound, base resin/(silica + difficultly soluble chromium compound), and silica/difficultly soluble compound. The coating of this resin composition may contain a polyiso-

cyanate compound as a hardener and further a silane compound as a crosslinking agent between the base resin and silica.

SUMMARY OF THE INVENTION

The present invention is made to eliminate the above-mentioned problems of the prior art and its object is to provide organic composite coated steel strip having improved corrosion resistance, weldability and coating adherence using a coating composition of a silica sol having a free silanol group in an organic solvent and a resin binder in which the dispersion of silica in the composition is restricted to some extent while keeping the silica sol compatible with the resin binder.

According to the present invention, there is provided an organic composite coated steel strip having improved corrosion resistance and weldability, comprising a zinc or zinc base alloy plated steel substrate, a chromate layer on the substrate containing up to 70 % by weight of Cr^{6+} based on the total chromium quantity, said chromate layer being coated in a weight of 5 to 500 mg/m^2 of elemental chromium, and an organic composite layer coated on said chromate layer having a dry weight of 0.2 to 3.0 g/m^2, comprising:

(A) an organic solvent dispersible silica; and
(B) an organic resin composition having a number average molecular weight of at least 2,000;

characterized in that said organic solvent dispersible silica has an organic deposit on its surface in an amount of up to 5.0% by weight, calculated as C, based on the total weight of the organic solvent dispersible silica and a specific surface area of 50 to 800 m^2/g; that said organic solvent dispersible silica consists of agglomerated secondary particles having an average particle size of 0.05-3.0 μm; and that the number of said secondary particles of said organic solvent dispersible silica ranges from $1x10^4$ to $1x10^9$ per square millimeter of a cross section of said organic composite layer.

Preferably, the organic solvent dispersible silica has a specific surface area of 100 to 400 m^2/g.

Preferably, the organic solvent of silica sol (A) has a total alkali metal content of up to 0.01% by weight. Alternatively, the silica of silica sol (A) has Al^{3+} adhered to the surface of silica in an amount of 0.1 to 20.0% by weight of elemental Al based on the total weight of the silica.

Preferably, organic resin composition (B) is based on an epichlorohydrin-bisphenol A epoxy resin having a number average molecular weight of at least 2,000.

Preferably, the coating composition contains silica sol (A) and organic resin composition (B) in such amounts that 10 to 100 parts by weight of silica sol is present per 100 parts by weight of the resin composition on a dry weight basis.

Preferably, organic resin composition (B) has a hydroxyl number of at least 50.

Preferably, said chromate layer is coated in a weight of 10 to 150 mg/m^2 of elemental chromium.

Preferably, said organic composite layer is coated by baking the coating composition at the maximum temperature of 100 to 200°C.

Preferably, the organic solvent of silica sol (A) is selected from the group consisting of n-butanol, isobutanol, ethyl cellosolve, butyl cellosolve, xylene, ethylene glycol, ethylene glycol n-propyl ether, dimethylacetamide, and mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described below in detail.

The starting stock material is zinc plated strip steel or zinc base alloy plated strip steel, which are sometimes referred to as zinc plated strip steel for brevity. The types of plating applied to steel substrates include all conventional zinc platings used for anti-corrosion purpose, for example, pure Zn plating, binary alloy platings such as Zn-Ni alloy platings with a nickel content of 8 to 16% by weight and Zn-Fe alloy platings with an iron content of 5 to 30% by weight, and ternary alloy platings such as Zn-Ni-Cr alloy platings and Zn-Co-Cr alloy platings. In addition, composite dispersion platings as typified by Zn-Co-Cr-Al_2O_3 platings are acceptable. These zinc platings may be applied by either electroplating or hot dipping.

The zinc platings are applied to steel substrates in ordinary coating weights for imparting corrosion resistance thereto. That is, the coating weight of zinc plating is not particularly limited insofar as its purpose is achievable.

The zinc plated steel substrate is subjected to chromate treatment primarily for imparting high corrosion resistance and secondarily for enhancing adherence or receptivity to an overlying coating.

The chromate layer is coated in a weight of 5 to 500 mg/m^2, preferably 10 to 150 mg/m^2 calculated as elemental chromium. If the chromium coating weight is less than 5 mg/m^2, some substrate areas can be left uncoated, which is undesirable for corrosion resistance and coating adherence. In excess of 500 mg/m^2, no further improvement in corrosion resistance is expectable and insulating film resistance is increased to such an extent as to deter welding and

electrophoretic deposition. Chromate layers in a coating weight of 10 to 150 mg/m^2 provide better performance with respect to corrosion resistance, adherence, weldability and electrophoretic deposition.

The chromate treatment may be conducted by any conventional techniques including coating chromate techniques using a roll coater, roll squeezer or the like, electrolytic chromate techniques, and reactive chromate techniques. The chromate bath contains a water-soluble chromium compound as a major component while any desired additives may be added thereto, for example, anions such as phosphate and fluoride ions, metal ions such as Zn, Ni and Co ions, and organic substances such as starch and methanol. It is also possible to add silica sol for improving corrosion resistance.

The proportion of Cr^{6+} in the chromate layer should be up to 70% by weight based on the total chromium quantity. If the proportion of Cr^{6+} exceeds 70% by weight, the chromate layer allows chromium to dissolve out during alkali degreasing.

On the chromate layer is applied a composite coating mainly composed of silica sol (A) and organic resin composition (B). The silica sol in the composite coating of the steel strip according to the present invention contributes to development of high corrosion resistance because silanol groups on the silica surface function to stabilize and hold zinc base corrosion products formed upon exposure to a corrosive environment.

Since it is impossible to apply silica sol alone to steel strips, the use of an organic resin binder is essential. The organic resin composition (B) used herein has a number average molecular weight Mn of at least 2,000 and desirably, a hydroxyl number H (KOH mg/resin g) of at least 50. Resins having an Mn of less than 2,000 are short in chain length and do not have a network structure. Such low molecular weight resins are ineffective as the silica binder and less compatible with silica sol, and can detract from corrosion resistance and coating adherence. The maximum number average molecular weight is not particularly limited. The preferred upper limit is set at 100,000 because the increased electric resistance of the coating can deter electrophoretic deposition and spot welding.

The hydroxyl group in the organic resin is a functional group contributing to adherence. If the hydroxyl number is less than 50, there is a possibility that (1) the coating fails to provide close adherence to the underlying chromate layer and (2) the coating fails to provide close adherence to an overlying electrophoretic film after cationic electrophoretic deposition. As a result, chromium will dissolve out of the chromate layer during alkali degreasing. If an organic composite coated steel strip on which an overlying film has been formed by electrophoretic deposition and a further overcoat (top coat) has been applied is exposed to a humid environment, the chromate to organic composite coating adherence and the organic composite coating to electrophoretic coating adherence become weak, resulting in coating separation. For these reasons, the organic resin should preferably have a hydroxyl number of at least 50. The maximum hydroxyl number is not particularly limited. However, if the hydroxyl number is extremely high, the resin can lose compatibility with silica sol and cause aggregation or agglomeration and gelation in preparing a coating composition.

The type of the organic resins used herein is not particularly limited. The organic resins include, for example, epoxy resins, acrylic resins, polyethylene resins, alkyd resins, and urethane resins, with the epoxy resins being preferred. The epoxy resins include glycidyl epoxy, glycidyl amine, aliphatic epoxide, and cycloaliphatic epoxide resins. Among these epoxy resins, epichlorohydrin-bisphenol A epoxy resins are preferred for toughness and corrosion resistance. They are commercially available, for example, as Epicoat 1010, 1009, 1007 and 1004 from Shell Kagaku K.K.

Epoxy resins having dialkanol amine added to their terminal oxirane group are also desirable. By incorporating more primary hydroxyl groups in an epoxy resin in a more stable fashion, silica is more firmly bound in the coating. The dialkanol amines used herein include diethanol amine, dipropanol amine, dibutanol amine, and the like.

If desired, the resin may be partially modified with urethane. Also, the resin may be blended with amine resins such as melamine and benzoguanamine as a crosslinking agent.

The silica sol (A) used herein is described in further detail.

The silica sol is an organic solvent dispersed silica sol which comprises silica dispersed in an organic solvent with a water content of up to 3.0% by weight wherein the silica has an organic deposit on its surface in an amount of up to 5.0% by weight, calculated as C, based on the total weight of the silica, an average particle size of 0.05 to 3.0 μm and a specific surface area of 50 to 800 m^2/g, preferably 50 to 400 m^2/g, more preferably 100 to 400 m^2/g.

As described in the preamble, several silicas including water dispersed silica sol, fumed silica, and hydrophobic silica are known to be blended in coating compositions of the type to which the present invention pertains. However, the water dispersed silica sol is unsuitable for use in coating compositions because it tends to immediately precipitate and gel when blended with the above-mentioned organic resin due to the face that water molecules are adsorbed to the surface of silica particles in hydration form.

The fumed silica is a fine powder of agglomerated silica particles having a siloxane bond therebetween and a silanol bond on the surface thereof. Several problems arise when fumed silica is blended in coating compositions. Mechanical shearing forces applied cause the coating composition to experience an acute rise of viscosity, making it difficult to apply the composition consistently on a commercial scale. The amount of fumed silica added to organic solvent is limited because thickening, precipitation and gelation occur with an increase of the amount.

The hydrophobic silica is also used to ensure that silica sol be dispersed in coating compositions. More particularly,

silanol groups on the surface of silica particles are substituted with organic groups to render the silica particles hydrophobic for dispersion in an organic solvent. The hydrophobic silica, when blended in coating composition, is successful in maintaining compatibility with the organic resin and providing excellent adherence of the coating, but has lost the ability of stably holding zinc corrosion products formed under the coating upon exposure to a corrosive environment because few free silanol groups are available on the particle surface. As a result, corrosion resistance is substantially poor.

The silica sol specified in the present invention is to eliminate the above-mentioned problems of the conventional types of silica sol. Silica is dispersed in an organic solvent having a water content of up to 3.0% by weight to provide compatibility with the resin composition. By limiting the amount of organic matter deposited on the silica surface to 5.0% by weight or less, calculated as elemental carbon, based on the total weight of the silica and the specific surface area of silica to 50 to 800 m^2/g, there are available free silanol groups on the silica surface, which contribute to a corrosion resistance improvement.

If the water content of the organic solvent is in excess of 3.0% by weight, the silica sol becomes less compatible with the resin composition. If more than 5% by weight, calculated as C, of organic matter is deposited on the silica surface, only few free silanol groups capable of stabilizing and holding corrosion products are available on the silica surface, resulting in a loss of corrosion resistance.

If the specific surface area of silica exceeds 800 m^2/g, the number of free silanol groups increases beyond the necessary level so that the silica sol tends to gel, making it difficult to prepare coating compositions and substantially impossible to apply to steel strip. With a specific surface area between 400 m^2/g and 800 m^2/g, there is a possibility that some coating compositions gel depending on a particular type of resin and are somewhat difficult to apply to steel strip. Therefore, the preferred upper limit of specific surface area is 400 m^2/g. With a specific surface area of less than 50 m^2/g, few free silanol groups are available on the silica surface, resulting in a loss of corrosion resistance. With a specific surface area in the range of from 100 to 400 m^2/g, the resulting coating exhibits a better profile of corrosion resistance and stability.

Further, the silica has an average particle size of 0.05 to 3.0 μm. The conventional silica sols generally contain silica particles of less than 0.05 μm size uniformly dispersed in a solvent without secondary agglomeration. We have discovered that such uniformly dispersed silica sol is detrimental to spot welding for the following reasons. In spot welding of coated steel strips, a welding electrode tip is quickly worn to reduce the electrode area and the welding current density therewith, failing to form a nugget. Silica acts as resistance during spot welding because it is not pyrolyzed at welding temperatures of about 700 to 800°C and has non-conductive nature although the organic resin can be pyrolyzed at such temperatures. Uniform distribution of silica in the coating layer minimizes the conduction path available for welding, inducing welding sparks and facilitating electrode wear of damage. That is, uniformly distributed silica adversely affects spot welding. For better welding performance, it is thus necessary to prevent uniform dispersion of silica to thereby provide a sufficient conduction path. Bearing this in mind, we have examined the distribution of silica in the organic composite coating layer to find that weldability can be substantially improved by controlling the number of silica particles per unit area on an arbitrary cross section of the organic composite coating layer. More specifically, weldability is improved by controlling the number of silica secondary particles to $1x10^9$ or less per square millimeter of a cross section of the organic composite layer because a sufficient conduction path is available during welding. If the number of silica secondary particles is less than $1x10^4$ per square millimeter of a cross section of the organic composite layer, weldability is high, but only a reduced number of silanol groups are available on the silica surface with a loss of corrosion resistance. The number of silica secondary particles should be $1x10^4$ or more per square millimeter of a cross section of the organic composite layer in order to ensure corrosion resistance. In order that the silica have a sufficient specific surface area to provide corrosion resistance and that a conduction path be available in the organic composite coating layer during welding, primary particles of silica in the coating composition should agglomerate into secondary particles which are present in the coating layer. Such an organic composite coating layer can be effectively produced by causing primary particles in the silica sol to undergo secondary agglomeration. Primary particles of silica should preferably agglomerate into secondary particles having an average particle size of at least 0.05 μm which allow for efficient welding. In turn, secondary particles having an average particle size of more than 3.0 μm are undesirable in applying the coating composition to uniform thickness. Means for inducing secondary agglomeration is not particularly limited. One preferred method capable of adjusting the particle size to the above-defined range is to limit the total alkali metal content in the organic solvent of the silica sol to 0.01% by weight or lower. It is also useful to attach Al^{3+} to the silica surface in an amount of 0.1 to 20.0% by weight of elemental aluminum based on the total silica weight. These two methods for secondary agglomeration mentioned above may be co-carried out.

The conventional silica sols generally contain about 0.05% by weight of alkali metal ions, for example, Na^+ in the form of Na_2O. If alkali metal oxides such as Na_2O are contained in the silica sol, there is formed an electrical double layer in which alkali metal ions such as Na^+ coordinate on the silica particle surface as counter ions and a hydration layer surrounds them, so that repulsion between silica particles maintains a colloidal state and uniform dispersion, preventing secondary agglomeration. However, by limiting the alkali metal content in the organic solvent to 0.01% by

weight or less, formation of an electrical double layer on the silica surface to provide electric charges is prevented, allowing primary particles to agglomerate into secondary particles having an average particle size of 0.05 to 3.0 μm.

The second useful method is attachment of Al^{3+} to the silica surface. If Al^{3+} is attached to the silica surface in an amount of 0.1% by weight or more, calculated as Al, based on the total silica weight, by adding basic aluminum chloride, for example, to silica sol, there result positively charged sites. Since the silica itself has a negative charge, the silica particles as a whole become neutral due to charge offsetting. However, attachment of Al^{3+} in an amount of more than 20.0% by weight, calculated as Al, based on the total silica weight causes undesirable displacement of corrosion resistance improving silanol groups. By attaching Al^{3+} to the silica surface in an amount of 0.1 to 20.0% by weight of elemental aluminum based on the total silica weight, formation of an electrical double layer on the silica surface to provide electric charges is prevented, allowing primary particles to agglomerate into secondary particles having an average particle size of 0.05 to 3.0 μm.

The silica sol used in the present invention is prepared by adding an organic solvent to a water dispersed silica sol and distilling off water therefrom until the water content reaches 3.0% by weight or lower. The organic solvent in which silica is dispersed should have a lower evaporation rate than water. Such organic solvents include n-butanol, isobutanol, ethyl cellosolve, butyl cellosolve, xylene, ethylene glycol, ethylene glycol n-propyl ether, dimethylacetamide alone and mixtures thereof. Moderate heating during distillation is recommended because excessive heating would cause silanol groups on the silica surface to react with an alcohol to form an ester, resulting in organic matter adhering to the silica surface in an amount of more than 5.0% by weight based on the total silica weight, adversely affecting corrosion resistance.

The coating composition preferably contains silica sol (A) and organic resin composition (B) in such amounts that 10 to 100 parts by weight of silica sol is present per 100 parts by weight of the resin composition on a dry basis. Corrosion resistance will be less desirable with less than 10 parts by weight of silica whereas with more than 100 parts by weight of silica, excess silica will not remain compatible with the resin composition so that the resulting coating composition becomes difficult to apply to steel strip.

The solvents for the coating composition include various organic solvents, for example, alcohols, ketones, esters, glycols, and ethers. For the stabilization of silica sol, it is desired that the coating composition have a water content of up to 1% by weight based on the total weight.

The coating composition may further contain a silane coupling agent, if desired, because linkages are formed between the base resin and silica so that silica is firmly bound. The conventional silane coupling agents include vinylsilanes, methacryloxysilanes, exposysilanes, aminosilanes, and mercaptosilanes. Among them, aminosilanes are unsuitable because they are incompatible with the resin composition used herein. In addition, addition of the silane coupling agent in excess amounts is detrimental to corrosion resistance because it bonds with a corrosion resistance improving silanol group on the silica surface to extinguish the useful silanol group. Therefore, it is recommended to add at most 20 parts by weight of silane coupling agent to 100 parts by weight of silica.

The coating composition as formulated above is applied to the chromate layer on the steel substrate to form an organic composite layer thereon by any desired commercial methods including roll coating and air knife coating methods. The organic composite layer has a dry weight of 0.2 to 3.0 g/m^2. Less than 0.2 g/m^2 is too thin to improve to corrosion resistance whereas more than 3.0 g/m^2 results in an increased film resistance which will adversely affect spot welding and electrophoretic deposition.

The organic composite layer is finally baked, preferably at the maximum temperature of 100 to 200°C on the strip surface. Baking temperatures of lower than 100°C are insufficient for drying and leave some solvent in the coating, leading to a loss of corrosion resistance. Baking temperatures of higher than 200°C will introduce yield elongation in the steel substrate so that stretcher strains are induced during subsequent pressing.

The organic composite coated steel strips of the present invention exhibit improved corrosion resistance and coating adherence, ensure satisfactory welding, and are useful in a variety of applications including automobile bodies.

EXAMPLE

Examples of the present invention are given below together with comparative examples by way of illustration and not by way of limitation. Unless otherwise stated, percents are by weight.

Examples

Low carbon cold rolled steel strips of 0.7 mm thick were coated with zinc or zinc alloy platings as shown in Table 4, subjected to coating chromate treatment using a roll coater as shown in Table 4, baked at the maximum strip temperature of 130°C, coated with coating compositions to form organic composite coatings as shown in Table 3 using a roll coater, baked at the maximum strip temperature of 160°C, cooled with water, and dried before they were examined by various tests. Tables 1 and 2 show the base resin and the silica sol of the coating compositions, respectively. All

the resin compositions and the coating compositions were prepared by typical methods (1) and (2) later described for coating composition No. 11.

In Table 2, the specific surface area of silica was measured by the BET method using N_2 gas, and the average particle size by the particle size distribution measurement by centrifugal settling. In Tables 2 and 3, ETC is ethyl cellosolve, NPC is ethylene glycol n-propyl ether, and BT is n-butanol. In Table 2, the organic deposit is expressed in % by weight of carbon based on the total silica weight, and the Al content is expressed in % by weight of aluminum based on the total silica weight. In Table 3, the amounts of the resin composition and the silica blended are on a dry basis. In Table 4, plating column, Zn-Ni is a Zn-Ni alloy plating containing 12% of nickel, plating A is a Zn-Ni-Cr alloy plating consisting of 12% of Ni, 1% of Cr and the balance of Zn, and plating B is a Zn-Co-Cr-Al_2O_3 dispersion plating consisting of 1% of Co, 0.8% of Cr, 1% of Al_2O_3, and the balance of Zn.

The number of silica secondary particles in a cross section of the coating layer reported in Table 4 was determined by slicing the coating layer to a thickness of 500 Å by means of a microtome, observing the slice under a transmission electron microscope, and counting the number of silica secondary particles per unit area.

The following performance evaluation tests were carried out.

Corrosion resistance

A combined cycle corrosion test was carried out, each cycle consisting of (1) salt water spraying for 4 hours with 5% NaCl solution at 35°C, (2) drying for 2 hours at 60°C, and (3) wetting for 2 hours at 95% RH and 50°C. The number of cycles repeated until red rust generation is reported.

Water resistant secondary adherence of coating

A coated specimen was subjected to phosphating treatment with PB L3020 (manufactured by Nihon Parkerizing K.K.), cationic electrophoretic deposition with Power Top U-600 (manufactured by Nihon Paint K.K) to 20 μm, baked at 170°C for 20 minutes, and overcoated with Lugabake White (manufactured by Kansai Paint K.K) to 35 μm, and baked at 140°C for 30 minutes. After immersion in pure water at 40°C for 10 days, the specimen was scribed with a cutter to define a pattern of 10x10 sections each 2 mm square. The percent of remaining coating sections after adhesive tape peeling was determined to evaluate the water resistant secondary adherence of the coating.

Chromium dissolution

A coated specimen was treated in four steps of degreasing, water washing, surface conditioning, and chemical conversion with a phosphate solution PB L3020 (manufactured by Nihon Parkerizing K.K.). The amount of chromium before and after the treatment were measured by a fluorescent X-ray analyzer to determine the amount of chromium dissolved out (mg/m^2).

Electrophoretic deposition

An electrocoat was applied to a coated specimen by conducting electricity at a voltage of 100 volts for 180 seconds in Power Top U-600 (manufactured by Nihon Paint K.K.) at 28°C, and baking at 170°C for 20 minutes. The number of gas pinholes in the electrocoat was counted. Evaluation was made according to the following criterion.

○: 0-6 pinholes/cm^2
Δ: 7-10 pinholes/cm^2
X: more than 10 pinholes/cm^2

Weldability

Using a welding torch of copper-chromium alloy having a tip diameter of 6 mm, continuous welding was carried out with a current of 9 kA and a resistance welding time of 10 Hz under a pressure of 200 kgf. The number of spot welds that could be made without interruption was counted until nugget has not come to be formed. Weldability was evaluated according to the following criterion.

○: more than 3,000 spots
Δ: 1,000-3,000 spots
X: less than 1,000 spots

(1) Preparation of terminally amine-modified epoxy resin varnish

A reactor equipped with a reflux condenser, stirrer, thermometer, and nitrogen gas inlet was charged with 300 grams of Epicoat 1009 (epoxy resin having an epoxy equivalent of 3,000, manufactured by Shell Kagaku K.K.) and 467 grams of ethyl cellosolve and heated to 80°C to form a homogeneous solution. To the solution was added dropwise 10.5 grams of diethanol amine over one hour. Reaction was continued for 3 hours at 80°C, obtaining an epoxy resin varnish having a solid content of 40%. The end of reaction was identified by detecting extinction of an epoxy group by chemical analysis.

(2) Preparation of solvent dispersed silica-containing coating composition

To 45 grams of the terminally amine-modified epoxy resin varnish obtained in (1) were added 60 grams of silica sol dispersed in ethyl cellosolve (specific surface area 150 m^2/g, water content 2%, Na_2O 0.005% or less, average particle size 0.3 μm, solids 20%) and 95 grams of ethyl cellosolve. The mixture was agitated for 10 minutes by means of a dispersion mixer, obtaining a solvent dispersed silica-containing coating composition (solids 15%).

Table 1:

Resin			
No.	Type	Number average molecular weight Mn	Hydroxyl number mg KOH/g
1	Epoxy (Epicoat 1009*)	3750	160
2	Terminally amine-modified No. 1	3800	185
3	30% urethane-modified No. 2	4000	160
4	Epoxy (Epicoat 1001*)	900	170
5	Acryl	8000	40

* Shell Kagaku K.K.

Table 2

Silica sol No.	Solvent	Silica type	Water Content wt%	Total alkali metal content wt%	Aℓ content wt%	Organic deposit on surface wt% (calculated as C)	Average particle size μm	Specific surface area m²/g	Silica content wt%	Stability
1	ETC	Wet	2.0	< 0.005	0.01	1.00	0.25	150	20	Good
2	ETC	Wet	2.0	< 0.005	0.01	1.00	0.30	350	20	Good
3	ETC	Wet	2.0	< 0.005	0.01	1.00	0.45	600	20	Partial settling
4	ETC	Wet	2.0	< 0.005	0.01	1.00	0.40	60	20	Good
5	ETC	Wet	2.0	< 0.005	0.01	1.00	0.30	40	20	Good
6	ETC	Wet	2.0	0.020	0.01	1.00	0.04	150	20	Good
7	ETC	Wet	2.0	< 0.005	0.01	6.00	0.50	150	20	Good
8	BT	Wet	2.0	< 0.005	0.01	1.00	0.20	150	20	Good
9	NPC	Wet	2.0	< 0.005	0.01	1.00	0.30	150	20	Good
10	ETC	Wet	4.0	< 0.005	0.01	1.00	—	150	20	Gel
11	water	Wet	80.0	< 0.005	0.01	< 0.01	0.01	150	20	Good
12	ETC	Dry	2.0	< 0.005	0.01	< 0.01	—	150	20	Gel
13	ETC	Wet	2.0	< 0.005	0.01	1.00	3.1	150	20	Good
14	ETC	Wet	2.0	0.02	0.05	1.00	0.02	150	20	Good
15	ETC	Wet	2.0	0.02	1.00	1.00	0.30	150	20	Good
16	ETC	Wet	2.0	0.02	22.0	1.00	0.50	150	20	Good

Table 3

Coating Composition No.	Resin		Silica		Solvent		Stability
	Type	Amount wt%	Type	Amount wt%	Type	Amount wt%	
1	1	9.0	1	6.0	ETC	85.0	Good
2	1	9.0	2	6.0	ETC	85.0	Good
3	2	9.0	3	6.0	ETC	85.0	Partial gelation
4	1	9.0	4	6.0	ETC	85.0	Good
5	1	9.0	5	6.0	ETC	85.0	Good
6	1	9.0	6	6.0	ETC	85.0	Good
7	1	9.0	7	6.0	ETC	85.0	Good
8	1	9.0	8	6.0	BT	85.0	Good
9	1	9.0	9	6.0	NPC	85.0	Good
10	1	9.0	11	6.0	water	85.0	Gel
11	2	9.0	1	6.0	ETC	85.0	Good
12	3	9.0	1	6.0	ETC	85.0	Good
13	4	9.0	1	6.0	ETC	85.0	Good
14	5	9.0	1	6.0	ETC	85.0	Good
15	1	14.0	1	1.0	ETC	85.0	Good
16	1	8.0	1	7.0	ETC	85.0	Good
17	1	14.5	1	0.5	ETC	85.0	Good
18	1	6.0	1	9.0	ETC	85.0	Partial gelation
19	1	9.0	13	6.0	ETC	85.0	Good
20	1	9.0	14	6.0	ETC	85.0	Good
21	1	9.0	15	6.0	ETC	85.0	Good
22	1	9.0	16	6.0	ETC	85.0	Good

Table 4 - 1

Example	Steel Strip		Chromate		Coating Composition		Number of silica secondary particles/ μm²	Form of silica	Corrosion resistance test cycles	Weldability	Chromium dissolution mg/m²	Secondary Electro-adherence coating
	Plating	Coating Weight g/m²	Cr** /total Cr	Coating Weight mg/m²	No.	Coating Weight mg/m²						
1	Zn-Ni	20	0.5	50	1	1.0	200	agglomeration	>200	○	< 1	100% ○
2	Zn-Ni	20	0.5	50	2	1.0	40	agglomeration	>200	○	< 1	100% ○
3	Zn-Ni	20	0.5	50	4	1.0	10	agglomeration	>200	○	< 1	100% ○
1*	Zn-Ni	20	0.5	50	5	1.0	50	dispersion	120	○	< 1	100% ○
2*	Zn-Ni	20	0.5	50	6	1.0	3800	dispersion	>200	×	< 1	100% ○
3*	Zn-Ni	20	0.5	50	7	1.0	80	agglomeration	100	○	< 1	100% ○
4	Zn-Ni	20	0.5	50	8	1.0	700	agglomeration	>200	○	< 1	100% ○
5	Zn-Ni	20	0.5	50	9	1.0	100	agglomeration	>200	○	< 1	100% ○
6	Zn-Ni	20	0.5	50	11	1.0	150	agglomeration	>200	○	< 1	100% ○
7	Zn-Ni	20	0.5	50	12	1.0	120	agglomeration	>200	○	< 1	100% ○
4*	Zn-Ni	20	0.5	50	13	1.0	100	agglomeration	120	○	< 1	40% ○
5*	Zn-Ni	20	0.5	50	14	1.0	150	agglomeration	100	○	< 1	100% ○
8	Zn-Ni	20	0.5	50	15	1.0	0.1	agglomeration	195	○	< 1	100% ○
9	Zn-Ni	20	0.5	50	16	1.0	800	agglomeration	>200	○	< 1	100% ○
10	Zn-Ni	20	0.5	50	17	1.0	0.005	agglomeration	190	○	< 1	100% ○
11	A	20	0.5	50	1	1.0	80	agglomeration	>200	○	< 1	100% ○
12	B	20	0.5	50	1	1.0	150	agglomeration	>200	○	< 1	100% ○
13	B	20	0.5	50	2	1.0	30	agglomeration	>200	○	< 1	100% ○

* Comparative Example

Table 4 - 2

Example	Steel Strip		Chromate		Coating Composition		Number of silica secondary particles/ μm^2	Form of silica	Corrosion resistance test cycles	Weldability	Chromium dissolution mg/m^2	Secondary Electoro-adherence coating
	Plating	Coating Weight g/m^2	Cr^{6+} /total Cr	Coating Weight mg/m^2	No.	Coating Weight mg/m^2						
6*	Zn-Ni	20	0.8	50	2	1.0	20	agglomeration	>200	○	25	100% ○
7*	Zn-Ni	20	0.5	600	2	1.0	40	agglomeration	>200	×	20	100% ×
14	Zn-Ni	20	0.5	50	2	0.3	5	agglomeration	>200	○	< 1	100% ○
15	Zn-Ni	20	0.5	50	2	2.8	20	agglomeration	>200	○	< 1	100% ○
8*	Zn-Ni	20	0.5	50	2	0.1	15	agglomeration	120	○	15	100% ○
9*	Zn-Ni	20	0.5	50	2	3.5	30	agglomeration	>200	×	< 1	100% ×
10*	Zn-Ni	20	0.5	50	19	1.0	0.02	agglomeration	160	○	< 1	100% ○
11*	Zn-Ni	20	0.5	50	20	1.0	2500	dispersion	180	×	< 1	100% ○
16	Zn-Ni	20	0.5	50	21	1.0	80	agglomeration	>200	○	< 1	100% ○
12*	Zn-Ni	20	0.5	50	22	1.0	200	agglomeration	150	○	< 1	100% ○
17	Zn-Ni	20	0.5	50	3	1.0	50	agglomeration	>200	○	< 1	100% ○

* Comparative Example

As is evident from Table 4, the examples falling with the scope of the present invention are organic composite

coated steel strips having improved corrosion resistance and weldability.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Claims

1. An organic composite coated steel strip having improved corrosion resistance and weldability, comprising:

   a zinc or zinc base alloy plated steel substrate;
   a chromate layer on the substrate containing up to 70% by weight of Cr^{6+} based on the total chromium quantity, said chromate layer being coated in a weight of 5 to 500 mg/m^2 of elemental chromium; and
   an organic composite layer coated on said chromate layer having a dry weight of 0.2 to 3.0 g/m^2, comprising:

   (A) an organic solvent dispersible silica; and
   (B) an organic resin composition having a number average molecular weight of at least 2,000;

   characterized in that said organic solvent dispersible silica has an organic deposit on its surface in an amount of up to 5.0% by weight, calculated as C, based on the total weight of the organic solvent dispersible silica and a specific surface area of 50 to 800 m^2/g; that said organic solvent dispersible silica consists of agglomerated secondary particles having an average particle size of 0.05-3.0 µm; and that the number of said secondary particles of said organic solvent dispersible silica ranges from $1x10^4$ to $1x10^9$ per square millimeter of a cross section of said organic composite layer.

2. The steel strip of claim 1, wherein the organic solvent dispersible silica has a specific surface area of 100 to 400 m^2/g.

3. The steel strip of claim 1 or 2, wherein the organic solvent dispersible silica (A) has Al^{3+} adhered to the surface of the organic solvent dispersible silica in an amount of 0.1 to 20.0% by weight of elemental Al based on the total weight of the organic solvent dispersible silica.

4. The steel strip of any one of claims 1 to3, wherein organic resin composition (B) is based on an epichlorohydrin-bisphenol A epoxy resin having a number average molecular weight of at least 2,000.

5. The steel strip of any one of claims 1 to 4 , wherein said organic composite layer contains the organic solvent dispersible silica (A) and the organic resin composition (B) in such amounts that 10 to 100 parts by weight of the organic solvent dispersible silica is present per 100 parts by weight of the organic resin composition on a dry weight basis.

6. The steel strip of any one of claims 1 to 5, wherein organic resin composition (B) has a hydroxyl number of at least 50.

7. The steel strip of any one of claims 1 to 6,
   wherein said chromate layer is coated in a weight of 10 to 150 mg/m^2 of elemental chromium.

Patentansprüche

1. Mit einem organischen Verbundüberzug versehenes Stahlband verbesserter Korrosionsfestigkeit und Schweißbarkeit, umfassend:

   ein mit Zink oder einer Legierung auf Zinkbasis plattiertes Stahlsubstrat;
   eine auf dem Substrat befindliche Chromatschicht mit, bezogen auf die gesamte Chrommenge, bis zu 70 Gew.-% Cr^{6+}, die in einer Menge von 5 - 500 mg/m^2 (als elementares Chrom) aufgetragen ist, und
   eine auf die Chromatschicht in einer Trockengewichtsmenge von 0,2 - 3,0 g/m^2 aufgetragene organische Verbundschicht aus

(A) einem in einem organischen Lösungsmittel dispergierbaren Siliciumdioxid und

(B) einer organischen Harzmasse eines anzahlgemittelten Molekulargewichts von mindestens 2000,

dadurch gekennzeichnet, daß das in einem organischen Lösungsmittel dispergierbare Siliciumdioxid auf seiner Oberfläche eine organische Ablagerung in einer Menge von bis zu 5,0 Gew.-% (berechnet als C), bezogen auf das Gesamtgewicht des in einem organischen Lösungsmittel dispergierbaren Siliciumdioxids, und eine spezifische Oberfläche von 50 - 800 m^2/g aufweist, daß das in einem organischen Lösungsmittel dispergierbare Siliciumdioxid aus agglomerierten Sekundärteilchen einer durchschnittlichen Teilchengröße von 0,05 - 3,0 µm besteht und daß die Anzahl der Sekundärteilchen an dem in einem organischen Lösungsmittel dispergierbaren Siliciumdioxid von 1 x 10^4 bis 1 x 10^9 pro mm^2 des Querschnitts der organischen Verbundschicht reicht.

2. Stahlband nach Anspruch 1, wobei das in einem organischen Lösungsmittel dispergierbare Siliciumdioxid eine spezifische Oberfläche von 100 - 400 m^2/g aufweist.

3. Stahlband nach Anspruch 1 oder 2, wobei an der Oberfläche des in einem organischen Lösungsmittel dispergierbaren Siliciumdioxids, bezogen auf dessen Gesamtgewicht, 0,1 - 20,0 Gew.-% Al^{3+} (berechnet als elementares Al) haftet (haften).

4. Stahlband nach einem der Ansprüche 1 bis 3, wobei die organische Harzmasse (B) auf einem Epichlorhydrin-Bisphenol A-Epoxyharz eines anzahlgemittelten Molekulargewichts von mindestens 2000 basiert.

5. Stahlband nach einem der Ansprüche 1 bis 4, wobei die organische Verbundschicht das in einem organischen Lösungsmittel dispergierbare Siliciumdioxid (A) und die organische Harzmasse (B) in solchen Mengen enthält, daß, auf Trockengewichtsbasis, auf 100 Gew.-Teile der organischen Harzmasse 10 - 100 Gew.-Teile an dem in einem organischen Lösungsmittel dispergierbaren Siliciumdioxid entfallen.

6. Stahlband nach einem der Ansprüche 1 bis 5, wobei die organische Harzmasse (B) eine Hydroxylzahl von mindestens 50 aufweist.

7. Stahlband nach einem der Ansprüche 1 bis 6, wobei die Chromatschicht in einer Menge von 10 - 150 mg/m^2 (als elementares Chrom) aufgetrgen ist.

Revendications

1. Un ruban en acier ayant un revêtement organique composite et présentant une résistance à la corrosion et une soudabilité améliorées, comportant :

un substrat en acier plaqué au zinc ou à un alliage à base de zinc ;

une couche de chromate sur le substrat, contenant jusqu'à 70 % en poids de Cr^{6+}, sur la base de la quantité totale de chrome, ladite couche de chromate constituant un revêtement suivant un poids de chrome élémentaire de 5 à 500 mg/m^2 ; et

une couche organique composite constituant un revêtement sur ladite couche de chromate, présentant un poids à sec de 0,2 à 3,0 g/m^2 , comportant :

(A) une silice dispersable dans un solvant organique ; et

(B) une composition de résine organique présentant un poids moléculaire moyen d'au moins 2.000 ;

caractérisé en ce que ladite silice dispersable dans un solvant organique comporte sur sa surface un dépôt organique suivant une quantité allant jusqu'à 5,0 % en poids, calculée en C, sur la base du poids total de la silice dispersable dans un solvant organique, et une aire de surface spécifique de 50 à 800 m^2/g ; en ce que ladite silice dispersable dans un solvant organique consiste en des particules secondaires agglomérées présentant une taille moyenne de particule de 0,05 - 3,0 µm; et en ce que le nombre desdites particules secondaires de ladite silice dispersable dans un solvant organique est situé dans la plage de 1x10^4 à 1x10^9 par millimètre carré d'une section

droite de ladite couche composite organique.

2. Le ruban d'acier de la revendication 1, dans lequel la silice dispersable dans un solvant organique présente une aire de surface spécifique de 100 à 400 m^2/g.

3. Le ruban d'acier de la revendication 1 ou 2, dans lequel la silice (A) dispersable dans un solvant organique comporte du Al^{3+} adhérant à la surface de la silice dispersable dans un solvant organique suivant une quantité de 0,1 à 20,0 % en poids de Al élémentaire, sur la base du poids total de la silice dispersable dans un solvant organique.

4. Le ruban d'acier de l'une quelconque des revendications 1 à 3, dans lequel la composition (B) de résine organique est basée sur une résine époxy épichlorohydrine-biphénol A présentant un poids moléculaire moyen d'au moins 2.000.

5. Le ruban d'acier de l'une quelconque des revendications 1 à 4, dans lequel ladite couche organique composite contient la silice (A) dispersable dans un solvant organique et la composition (B) de résine organique suivant des quantités telles que 10 à 100 parties en poids de la silice dispersable dans un solvant organique sont présentes pour 100 parties en poids de la composition de résine organique sur une base de poids à sec.

6. Le ruban d'acier de l'une quelconque des revendications 1 à 5, dans lequel la composition (B) de résine organique présente un nombre d'hydroxyles d'au moins 50.

7. Le ruban d'acier de l'une quelconque des revendications 1 à 6, dans lequel ladite couche de chromate constitue un revêtement suivant une quantité de chrome élémentaire de 10 à 150 mg/m^2 .